

Cross reference to related applications

5 This application claims the priority of European patent application 00 105 910.4, filed March 22, 2000, the disclosure of which is incorporated herein by reference in its entirety.

10 Background of the invention

The present invention relates to an admixture for cementitious compositions which reduces the drop in fluidity with time.

15 High range water reducing admixtures, also known as superplasticisers, for cementitious compositions such as cement pastes, mortars or concretes, are quite well known and used already since the late 1960's. They improve the workability of the composition and allow a  
20 reduction of the water to cement ratio. The improvement of workability can also be attained by use of more water but this influences negatively the properties of the cementitious composition in the hardened state e.g. the tensile and compressive strengths, resistance to frost,  
25 resistance to deicing salts, waterproofness, resistance to abrasion and chemical durability. Examples for high range water reducers are salts of naphthalene sulfonic acid condensates or salts of melamine sulfonic acid condensates. These polymers suffer from the problem of  
30 drastic loss of fluidity of the cementitious composition, with time. This loss of workability is a big problem for applications where the cementitious composition like concrete, has to be transported over longer distances. Other examples of superplasticizers are copolymers of  
35 maleic acid or polyglycol esters thereof as mentioned in EP 291073, EP 373621, EP 306449, EP 850894 which all show reduced slump-loss. But maleic acid copolymers are known

to suffer from the problem of strong retardation of the hardening of the cementitious composition. In the last years new superplasticisers, copolymers of (meth)acrylic acid with polyalkyleneoxide side chains, so called comb polymers, were developed which have very high water reduction. But if this water reduction of more than 20% is realised, the composition suffers from slump-loss e.g. loss of fluidity with time.

In view of the foregoing disadvantages of the prior art a novel admixture for cementitious compositions is needed which reduces the drop in fluidity of superplasticised cement pastes, mortars or concretes.

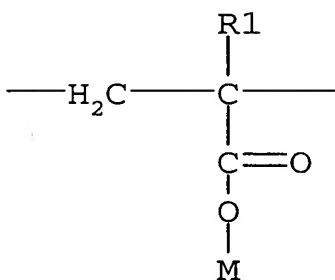
#### Brief summary of the invention

Hence, it is a general object of this invention to provide a polymer and an admixture comprising same for cementitious compositions which reduce the drop in fluidity (called slump-loss) with time without excessive retardation of the hardening. The present invention is based on the discovery that the aforementioned problems can be solved by use of a polymer, and preferably an admixture comprising said polymer (also referred to as polymer B) and at least one further polymer, designated polymer A, wherein the polymer B of the present invention comprises side chains of which at least 10 weight-% can be cleaved in alkaline medium at a pH of from 8-14. This polymer, and in particular the admixture, can drastically reduce the slump loss of cementitious compositions.

The polymer of the present invention  
comprises

a mole-% of structural unit A of formula I

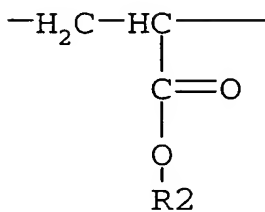
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I

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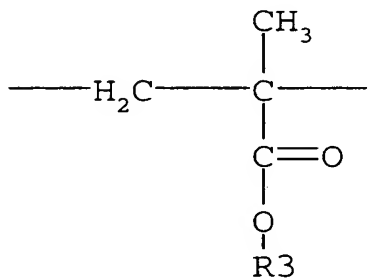
b mole-% of structural unit B of formula II



II

15

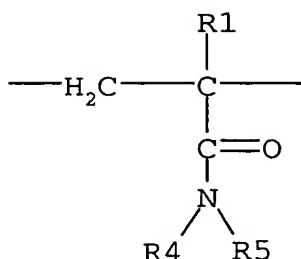
c mole-% of structural unit C of formula III



III

20

d mole-% of structural unit D of formula IV

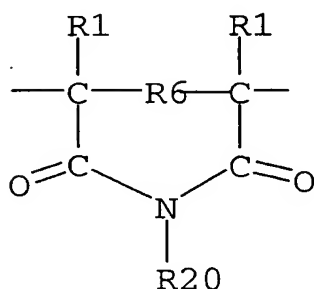


IV

5

and

e mole-% of structural unit E of formula V



10

V

wherein each R1 independently from each other  
15 represents a hydrogen atom or a methyl group or mixtures  
thereof (wherever the expression "mixtures thereof"  
occurs in connection with the specification of  
substituents, it means that structural units of a  
specific kind with a specific substituent can be present  
20 simultaneously with one or more other structural units of  
the same kind but with other specific substituents,  
and/or that, where one structural unit comprises several  
substituents identically designated, said substituents  
can have different meanings in one and the same  
25 structural unit);

M represents a hydrogen atom, a metallic cation, an ammonium or organic ammonium cation (such as e.g. alkyl and/or alkanol substituted cations with at least one such substituent, in particular C<sub>1</sub> to C<sub>4</sub> alkyl and/or C<sub>1</sub> to C<sub>4</sub> alkanol substituted ammonium cations) or mixtures thereof;

R<sub>2</sub>, R<sub>20</sub> and R<sub>3</sub> independently from each other represent a C<sub>1</sub>-C<sub>12</sub> alkyl- or cycloalkyl group, a C<sub>2</sub>-C<sub>12</sub> hydroxyalkyl group or (R<sup>7</sup>O)<sub>z</sub>R<sup>8</sup> in which O represents an oxygen atom, R<sup>7</sup> represents a C<sub>2</sub>-C<sub>3</sub> alkylene group or mixtures thereof, R<sup>8</sup> represents a hydrogen atom, a C<sub>1</sub>-C<sub>12</sub> alkyl- or cycloalkyl group, a C<sub>2</sub>-C<sub>12</sub> hydroxyalkyl group, or an unsubstituted or substituted aryl group and z represents a number from 1-250; whereby R<sub>2</sub>, R<sub>3</sub> and R<sub>20</sub> may be mixtures thereof,

R<sub>4</sub> and R<sub>5</sub> represent independently from each other a hydrogen atom or a substituent as defined for R<sub>2</sub>, and R<sub>4</sub> and R<sub>5</sub> may form together a ring structure of which N is part of, this ring structure may further contain other hetero atoms like another nitrogen, sulfur or oxygen atom, or mixtures thereof;

R<sub>6</sub> is a single bond or a methylene group, a, b, c, d and e represent numbers where the sum of a+b+c+d+e=100 and b is a number from 10-90, c is a number from 0-85, d is a number from 0-50 and e is a number from 0-10 and a is 100 - (b+c+d+e), whereby a is at least 5.

In one preferred embodiment of the present invention, the sum of e and d is preferably a value of more than 0, more preferably between 0.01 and 50, most preferably between 0.01 and 2.

Another preferred embodiment of the present invention comprises a polymer as defined above in which at least 0.5 mole-%, more preferred 5-100 mole-% and most preferred 50-100 mole-% of the residues R<sub>2</sub> of structural units B of formula II are -(R<sup>7</sup>O)<sub>z</sub>R<sup>8</sup> with R<sup>7</sup>, z and R<sup>8</sup> as defined above.



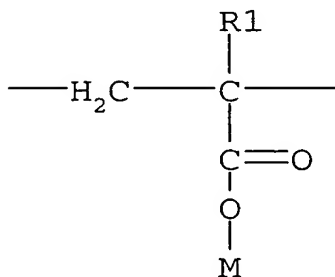
### Detailed description of the invention

This invention relates to a polymer and an  
5 admixture comprising at least one polymer A and at least  
one polymer of the present invention, whereby the polymer  
of the present invention comprises side chains of which  
at least 10 weight-% can be cleaved in alkaline medium at  
a pH of from 8-14. This polymer, and in particular said  
10 admixture can drastically reduce the slump-loss of  
cementitious compositions.

The side chains of the polymer of the present  
invention may be connected to the backbone by ester  
linkages. Said polymer may further contain side chains,  
15 which are connected to the backbone by amide groups. Side  
chains which are cleavable in alkaline medium are e.g.  
ester linkages like in polymerised acrylic esters. Not  
cleavable in the aforementioned manner are esters like in  
polymerised methacrylic esters. Furthermore side chains  
20 which are connected to the backbone by amide or imide  
linkages are not considered as cleavable in the idea of  
this patent.

The polymer of the present invention  
comprises  
25

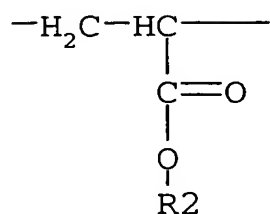
a mole-% of structural unit A of formula I



I

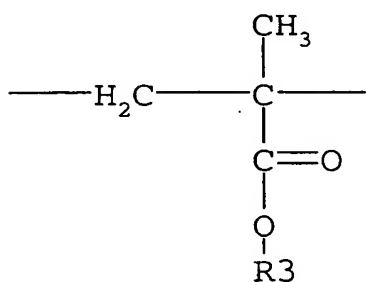
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b mole-% of structural unit B of formula II



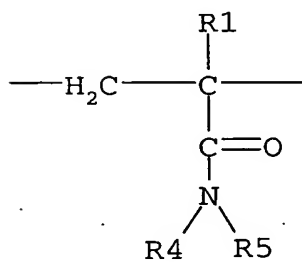
II

5 c mole-% of structural unit C of formula III



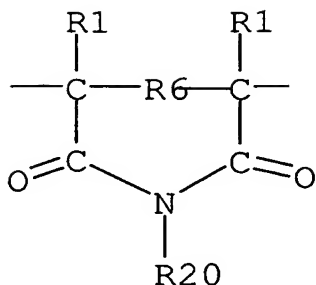
III

10 d mole-% of structural unit D of formula IV and



IV

e mole-% of structural unit E of formula V



v

5                    wherein each R1 independently from each other represents a hydrogen atom or a methyl group or mixtures thereof;

10                    M represents a hydrogen atom, a metallic cation, an ammonium or organic ammonium cation (such as e.g. alkyl and/or alkanol substituted cations with at least one such substituent, in particular C<sub>1</sub> to C<sub>4</sub> alkyl and/or C<sub>1</sub> to C<sub>4</sub> alkanol substituted ammonium cations) or mixtures thereof;

15                    R2, R20 and R3 independently from each other represent a C<sub>1</sub>-C<sub>12</sub> alkyl- or cycloalkyl group, a C<sub>2</sub>-C<sub>12</sub> hydroxyalkyl group or (R7O)<sub>z</sub>R8 in which O represents an oxygen atom, R7 represents a C<sub>2</sub>-C<sub>3</sub> alkylene group or mixtures thereof, R8 represents a hydrogen atom, a C<sub>1</sub>-C<sub>12</sub> alkyl- or cycloalkyl group, a C<sub>2</sub>-C<sub>12</sub> hydroxyalkyl group, 20 or an unsubstituted or substituted aryl group and z represents a number from 1-250, whereby R2, R3 and R20 may be mixtures thereof;

25                    R4 and R5 represent independently from each other a hydrogen atom or a substituent as defined for R2, and R4 and R5 may form together a ring structure of which N is part of, this ring structure may further contain other hetero atoms like another nitrogen, sulfur or oxygen atom, or mixtures thereof;

                    R6 is single bond or a methylene group,

a, b, c, d and e represent numbers where the sum of  $a+b+c+d+e=100$  and b is a number from 10-90, c is a number from 0-85, d is a number from 0-50 and e is a number from 0-10 and a is  $100 - (b+c+d+e)$ , whereby a is at least 5.

In one preferred embodiment of the present invention the sum of e and d is preferably a value of more than 0, more preferably between 0.01 and 50, most preferably between 0.01 and 2.

Another preferred embodiment of the present invention comprises a polymer as defined above in which at least 0.5 mole-%, more preferred 5-100 mole-% and most preferred 50-100 mole-% of the residues R<sup>2</sup> of structural units B of formula II are  $-(R^7O)_zR^8$  with R<sup>7</sup>, z and R<sup>8</sup> as defined above.

The polymer of the present invention, as defined above, may contain side chains of formula VI which are connected to the backbone by amide or ester groups.



In formula VI O represents an oxygen atom and A<sup>1</sup> and B<sup>1</sup> represent independently from each other a C<sub>2</sub>-C<sub>3</sub> alkylene group and A<sup>1</sup> ≠ B<sup>1</sup> and

R<sub>9</sub> represents a hydrogen atom, a C<sub>1</sub>-C<sub>12</sub> alkyl- or cycloalkyl group, a C<sub>2</sub>-C<sub>12</sub> hydroxyalkyl group, or an unsubstituted or substituted aryl group and x represents a number from 1-250 and y represents a number from 0-250 and the sum of x and y is a number of 1-250 and the order (A<sup>1</sup>O) and (B<sup>1</sup>O) is random, alternating or blockwise.

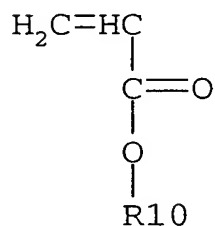
The amount of these side chains of formula VI in the polymer is preferably greater than 0.5 weight-%

more preferred 5-99 weight-% and most preferred 50-99 weight-% of the polymer.

The inventive polymer comprises 5-90 mole-% more preferably 20-80 mole-% of structural unit A of formula I and 10-90 mole-% more preferably 15-70 mole-% of structural unit B of formula II and 0-85 mole-% of structural unit C of formula III and 0-50 mole-% more preferably 0-20 mole-% of structural unit D of formula IV and 0-10 mole-% of structural unit E of formula V .

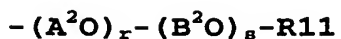
The polymer of the present invention as defined above may be produced by copolymerisation reactions as described in standard literature. The monomers resulting in structural unit A of formula I in said polymer are selected from the group comprising acrylic acid and methacrylic acid which may be fully or partly neutralised before or after the polymerisation with an alkaline substance. Examples for this alkaline substance are metal hydroxides like alkali metal and alkaline earth metal hydroxides, aluminum hydroxid or oxide hydroxide, tin or zinc compounds, ammonia, alkyl amines or hydroxyalkyl amines.

The monomers resulting in structural unit B of formula II in the polymer B are acrylic esters. Examples, but not exclusive, of the acrylic esters are C<sub>1</sub>-C<sub>12</sub> alkyl or cylcoalkyl acrylates, C<sub>2</sub>-C<sub>12</sub> hydroxyalkyl acrylates or hydroxy or alkyl terminated polyalkyleneglycole acrylates as shown in formula VII



VII

with R10 representing a polyalkyleneglycole chain shown  
5 in formula VIII



VIII

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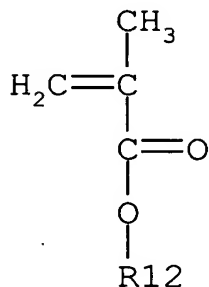
wherein O represents an oxygen atom and A<sup>2</sup> and B<sup>2</sup> represent independently from each other a C<sub>2</sub>-C<sub>3</sub> alkylene group and A<sup>2</sup>≠B<sup>2</sup> and

15 R11 represents a hydrogen atom, a C<sub>1</sub>-C<sub>12</sub> alkyl- or cycloalkyl group, a C<sub>2</sub>-C<sub>12</sub> hydroxyalkyl group, or an unsubstituted or substituted aryl group and r represents a number from 1-250 and s represents a number from 0-250 and the sum of r and s is a number of 1-250 and the order (A<sup>2</sup>O) and (B<sup>2</sup>O) is random, alternating or  
20 blockwise.

Monomers VII with different R10 may be used in combinations with each other.

The monomers resulting in structural unit C of formula III in the polymer of the present invention  
25 are methacrylic esters. Examples but not exclusive, of these methacrylic esters are C<sub>1</sub>-C<sub>12</sub> alkyl or cycloalkyl methacrylates, C<sub>2</sub>-C<sub>12</sub> hydroxyalkyl methacrylates, or alkyl terminated polyalkyleneglycole methacrylates as shown in formula IX

30



IX

with R12 representing a polyalkyleneglycol chain shown in formula X

5



wherein O represents an oxygen atom and A<sup>3</sup> and B<sup>3</sup> represent independently from each other a C<sub>2</sub>-C<sub>3</sub> alkylene group and A<sup>3</sup> ≠ B<sup>3</sup>, and

R13 represents a hydrogen atom, a C<sub>1</sub>-C<sub>12</sub> alkyl- or cycloalkyl group, a C<sub>2</sub>-C<sub>12</sub> hydroxyalkyl group, or an unsubstituted or substituted aryl group and t represents a number from 1-250 and u represents a number from 0-250 and the sum of t and u is a number of 1-250 and the order (A<sup>3</sup>O) and (B<sup>3</sup>O) is random, alternating or blockwise.

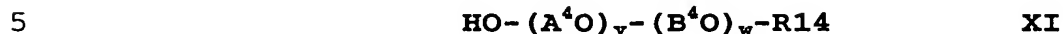
Monomers IX with different R12 may be used in combinations with each other.

The monomers resulting in structural unit D of formula IV in the polymer of the present invention are acrylamides or methacrylamides or N-substituted acrylamides or methacrylamides. Examples, but not exclusive, of these methacrylic amides are methoxypolyalkyleneglycole acrylamides, methoxypolyalkyleneglycole methacrylamides, acryl or methacrylamides of dicyclohexylamine, acryl or methacrylamides of oxazolidine.

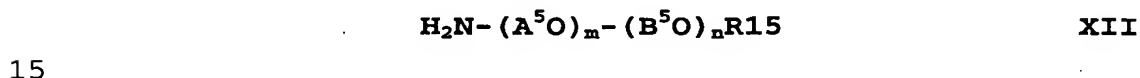
The polymerisation of the mentioned monomers may be carried out in bulk or in solution, initiated by a polymerisation initiator. Further chain transfer agents and redox-initiator systems may be used.

The inventive polymers as defined above may be produced by reacting a polycarboxylic acid or a C<sub>1</sub>-C<sub>5</sub>-ester thereof or a partly neutralised polycarboxylic acid, having all a number average molecular weight of

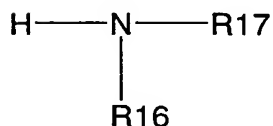
from 500 to 20'000 with a monofunctional polyalkyleneglycol-monoalkylether, represented by formula XI



and optionally  
10 a monofunctional  $\alpha$ -amino-polyalkyleneglycol- $\omega$ -alkylether, represented by formula XII



and/or, optionally  
a primary or secondary amine, represented by formula XIII  
20



XIII

25 wherein O represents an oxygen atom and A<sup>4</sup>, A<sup>5</sup>, B<sup>4</sup> and B<sup>5</sup> represent independently from each other a C<sub>2</sub>-C<sub>3</sub> alkylene group and A<sup>4</sup>≠B<sup>4</sup> and A<sup>5</sup>≠B<sup>5</sup>. R14 and R15 independently represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group and v and m represent a number from 1-250 and w and  
30 n represent a number from 0-250 and the sum of v and w and the sum of m and n is a number of 1-250 and the order (A<sup>4</sup>O) and (B<sup>4</sup>O) respectively of (A<sup>5</sup>O) and (B<sup>5</sup>O) is random, alternating or blockwise.

R16 and R17 independently from each other  
35 represent a hydrogen atom or an C<sub>1</sub> - C<sub>4</sub> alkyl group, or

oxyalkylen groups of the structure  $R18-(O-R19)_p-$ , where R18 independently represents a  $C_1 - C_4$  alkyl rest and R19 independently represents a  $C_2 - C_3$  alkylene group or a mixture thereof, wherein the mixture may be formed by  
5 either random, alternating or block addition,

R16 and R17 represent also cyclic derivatives such as aliphatic  $C_3 - C_8$  rings, and R16 and R17 together may form a heterocyclic ring structure wherein N is a part of. This heterocyclic ring may contain in addition  
10 to the N atom further N, S or O atoms.

Examples, but not limiting, for polycarboxylic acids which can be used for the production of the polymer of the present invention are polyacrylic acid, copolymers of acrylic acid with methacrylic acid,  
15 homo or copolymers of acrylic  $C_1-C_5$ -esters, or copolymers of methacrylic acid with  $C_1-C_5$  acrylic esters. The term polyacarboxylic acid further comprises also partly neutralised polymers.

Part of the side chains in the inventive  
20 polymer is cleaved in alkaline medium.

As alkaline medium a medium is meant, which may be an aqueous liquid, paste, slurry, emulsion or a dispersion of a pH from 8-14.

Example for an alkaline medium is the liquid  
25 phase of a cement slurry.

The admixture for preventing drop in fluidity of cementitious admixtures of this invention contains besides the inventive polymer a polymer A which is a cement dispersing agent preferably of the group  
30 consisting of sulfonated melamine condensates, sulfonated naphthalene condensates, lignosulfonates, substituted maleamid-vinyl-copolymers and acrylic or methacrylic copolymers with polyalkyleneoxide side chains, or mixtures thereof.

35 A preferred admixture for example comprises a polymer of the present invention consisting of 40-80 mole-% of structural unit A of formula I, 20-70 mole-% of

structural unit B of formula II, 0-50 mole-% of structural unit C of formula III, 0-20 mole-% of structural unit D of formula IV and 0-5 mole-% of structural unit E of formula V and polymer A is a copolymer of (meth)acrylic acid with polyalkyleneoxide methacrylate.

The solid weight ratio of polymers A to the polymers of the present invention usually is from 0.1:10-10:1 and preferably from 1:10-10:1.

The addition of polymer A and the inventive polymer to the cementitious composition may be in solid form or as liquid admixture or in an adsorbed form on a powder material. The addition of said two polymers can be performed combined in one admixture or they can be added separately to the cementitious composition. Polymer A and the polymer of the present invention may furthermore be added at the same time or at different times to the cementitious composition.

The cementitious composition according to the present invention comprises cement, the polymer or cement admixture of the present invention and water and is, for example used as cement paste, mortar or concrete. Examples of cement which can be used include many kinds of Portland cement like ordinary Portland cement, high early strength or moderate heat Portland cement, white cement, blended cements which contain fly ash, slag, puzzolanic materials, carbonaceous materials, silica fume, burnt oil shale, metakaolin or gypsum.

The cement composition of the present invention may further comprise conventional admixtures like plasticisers, superplasticisers, air entraining admixtures, defoamers, retarders, set accelerators, hardening accelerators, hydrophobising or shrinkage reducing admixtures or corrosion inhibitors.

### Production Examples

The following examples describe the synthesis of the polymer of the invention.

5                   It is clear for the averagely skilled person that, if polyalkylene oxides or their derivatives are used, the number of alkylene oxide units is a mean value of a molecular number distribution and the mentioned molecular weights are the mean molecular weights of the  
10                   used polymer.

#### Example 1 - for producing polymer E1

                  A one litre reactor, equipped with a  
15                   mechanical stirrer, a dropping funnel, a reflux condenser, a thermometer and two inlet tubes was charged with 308 g deionized water.

                  A monomer solution was prepared of 32.4 g acrylic acid, 57 g of a methoxy polyethyleneglycol  
20                   acrylate with 11 units of ethyleneglycol, 160 g of a polyethyleneglycol methacrylate with 23 units of ethyleneglycol and 110 ml deionized water and filled in the dropping funnel.

                  A solution A was prepared of 10.8 g sodium  
25                   persulfate in 40 g deionized water. A solution B was prepared of 8.0 g sodium disulfite in 40 g deionized water.

                  The reactor was heated and at a temperature of the water of 80°C the monomer solution was added from  
30                   the dropping funnel and the solutions A and B were added separately with a tube-pump within 4 hours at 80 °C.

                  After the additions the mixture was stirred at 80 ° C until the peroxide test was negative. After cooling to room temperature, the pH of the polymer  
35                   solution was adapted to 5 by addition of 22.7 g 50% sodium hydroxide solution.

Example 2-5 - for producing polymer E2-E5

5       The polymers are produced in the same manner  
as described in example 1. The monomers used and their  
dosages in grams are listed in table 1.

Comparison examples 1-3 - for producing  
polymer C1-C3

10       The polymers are produced in the same manner  
as described in example 1. The monomers used and their  
dosages in grams are listed in table 1.

**Table 1**

Example	AS	MAS	PEO 6A	MPEO 11A	MPEO 1000MA	MPEO 2000MA	SPS	SDS	Total water	NaOH 50%
Polymer E2	18.0		110.7				9.0	6.7	239	12.3
Polymer E3	18.0			172.0			8.5	6.3	353	18.8
Polymer E4		43.0	133.0		106.8		17.2	12.4	525	18.2
Polymer E5	36.0		133.0			208.0	11.4	8.0	700	22.0
Polymer C1		34.5				165	8.2	5.9	370	33.5
Polymer C2		17.2	26.5		106.8		5.9	4.2	280	6.3
Polymer C3		25.8			106.8		6.9	4.9	246	23.1

- 5 AS.....acrylic acid  
 MAS.....methacrylic acid  
 PEO 6A.....hydroxy polyethyleneglycol acrylate with 6  
 units of ethyleneglycol  
 MPEO 11A.....methoxy polyethyleneglycol acrylate with 11  
 10 units of ethyleneglycol  
 MPEO 1000MA, MPEO 2000MA.....methoxy polyethyleneglycol  
 methacrylate with mol. weight of the polyethyleneglycol  
 chain of 1000 resp. 2000  
 SPS.....sodium persulfate  
 15 SDS.....sodium disulfite

Example 6 - for producing polymer E6

- 20 160 g of a 50% aqueous solution of a 4000  
 molecular weight poly(acrylic acid) and 7.5 g 50 wt.%  
 sulfuric acid were placed in a glass reactor fitted with  
 a thermometer, a stirrer, a gas inlet tube and a  
 distillation assembly. The solution was heated to 70°C  
 25 and 140 g of a 350 number average molecular weight  
 polyethyleneglycol-monomethylether and 200 g of a 2000

number average molecular weight  $\alpha$ -amino-polyethylene-glycol- $\omega$ -methylether were added.

The mixture was heated up under a steady stream of nitrogen and kept at 165°C. After 6 h stirring at 165°C the mixture was cooled down. At 90°C 630 g water were added.

Examples 7-14 - for producing polymers E7-E14

The polymers were produced in the same manner as described in example 6 but with the amounts of reactants in grams listed in table 2.

**Table 2**

All values in grams (except time in hours and minutes)

Example	PAS 4000	SS 50%	PEG 350MME	PEG 500MME	PEG 1000MME	A-PEG 500MME	A-PEG 2000MM E	Reaction Time at 165°C (hh:mm)
Polymer E7	160	7.5	0	175	0	26	0	7:30
Polymer E8	160	7.5	123	0	0	100	0	4:00
Polymer E9	160	7.5	0	0	400	0	0	7:00
Polymer E10	160	7.5	0	0	300	52	0	6:00
Polymer E11	160	7.5	0	0	380	10	0	6:00
Polymer E12	160	7.5	123	0	0	0	100	7:00
Polymer E13	160	5.0	200	0	0	0	0	3:00
Polymer E14	160	7.5			350	26	0	6:00

PAS 4000: 50% aqueous solution of a 4000 molecular weight poly(acrylic acid)

SS 50%: sulfuric acid 50wt% in water

PEG 350MME: polyethyleneglycol-monomethylether of average molecular weight of 350

PEG 500MME: polyethyleneglycol-monomethylether of average molecular weight of 500

PEG 1000MME: polyethyleneglycol-monomethylether of average molecular weight of 1000

A-PEG 500MME: alpha-amino-polyethyleneglycol-omega-methylether of average molecular weight of 500

5 A-PEG 2000MME: alpha-amino-polyethyleneglycol-omega-methylether of average molecular weight of 2000

10 **Cleavage of side chains of polymers in alkaline medium**

To follow the cleavage of side chains of polymer B in alkaline medium the HPLC was used to measure  
15 the amount of free polyalkyleneglycol in the solution.

Preparation of the alkaline solution:

100 g water and 100 g normal Portland cement were blended for 30 minutes and the solution was filtered off with the aid of a paper filter.

20 The alkaline solution had a pH of 12.9 and corresponds to the solution of a cementitious composition with a water/cement ratio of 1.0.

Side chain stability:

25 1.0 g of polymer with 40% solids content was dissolved in 100 ml of the aforementioned alkaline solution and analysed by HPLC technique.

The amount of polyalkylene glycole in the solution was measured at different times.

30 The results are listed in table 3. The percentage of cleaved side chains means, the g of side chains that have been cleaved off the main chain per 100 g of all side chains.

**Table 3**

Polymer	Weight % side chains in polymer	Weight % of side chains cleaved after 40 min	Weight % of side chains cleaved after 2 hours	Weight % side chains cleaved after 24 hours
Polymer E1	80	16	20	25
Polymer E2	71	39	50	56
Polymer E3	79	41	43	76
Polymer E6	81	13	16	34
Polymer E7	72	22	31	66
Polymer E13	71	34	52	90
Polymer E14	83	21	37	93
Polymer C3	75	0	0	0
Polymer C2	81	4	4	4

5

## Application Tests

10

### Mortar tests

### Materials used

15

Normal Portland cement type I	750 g
carbonateous filler	150 g
fine sand 0-1.2 mm	950 g
sand 1.2-4 mm	800 g
sand 4-8 mm	1250 g

20

### Mixing procedure

5 Filler, sand and cement were blended in a Hobart type mortar mixer for 60 seconds, the water containing the admixtures was added and the mortar mechanically kneaded for 3 minutes.

### Measurement of plasticity

10 Flow table spread (a measure of the flowability of the mortar) was measured according German Standard DIN 18555 part 2 using the equipment described in German Standard DIN 1060 part 3. The measurement was repeated after 30 and 60 minutes with 30 seconds mixing  
15 of the mortar. The decrease of the flow with time is a measure of the loss of fluidity of the mortar.

### Results

20 Results of the mortar tests of the inventive admixtures and comparison admixtures is summarised in table 4.

### Polymers A in table 4:

25 Polymer A1 is a modified maleamide-vinyl-copolymer;

Polymers A2, and A3 are copolymers of methacrylic acid with methacrylic ester of methylpolyethyleneglycol.

30 The W/C ratio is the weight of the cement divided by the weight of the water.

All admixtures were used as 35% solutions.

If necessary, the polymer solutions were defoamed with 0.2% triisobuty-phosphate.

**Table 4**

Polymer A	Polymer of the invention	Dosage % on cement	W/C	Flow Table Spread (mm)		
				0 min	after 30 min	after 60 min
Polymer A1		1.0	0.44	190	167	144
Polymer A1	Polymer E3	0.7/0.7	0.44	182	170	173
Polymer A1	Polymer E14	0.6/0.6	0.44	190	189	176
Polymer A1	Polymer C3	0.8/0.2	0.44	212	157	142
Polymer A2	-	1.0	0.40	186	163	157
Polymer A2	Polymer E7	0.25/0.75	0.40	184	190	176
Polymer A2	Polymer E6	0.7/0.5	0.40	180	173	171
Polymer A2	Polymer C1	0.5/0.5	0.40	164	148	143
Polymer A2	Polymer C2	0.75/0.25	0.40	168	163	136
Polymer A3		1.0	0.41	187	143	141
Polymer A3	Polymer E3	0.8/0.2	0.41	207	208	187
Polymer A3	Polymer E1	0.4/0.5	0.41	186	176	174
Polymer A3	Polymer E13	0.7/1.1	0.41	176	167	170

5                      The results of the mortar tests listed in table 4 show clearly the reduction of slump-loss by using polymer A and the polymer of the present invention together.

10

#### Concrete Tests

#### Materials used

15	Normal Portland Cement type I	7.5 kg
	Lime stone filler	1.5 kg
	Sand 0-1.2mm	9.5 kg
	Sand 1.2-4.0 mm	8.0 kg
	Sand 4.0-8.0 mm	4.5 kg
20	Gravel 8-16 mm	9.5 kg
	Gravel 16-32 mm	17.0 kg
	Sand and gravel washed and dried	

### Measurement of plasticity in concrete

Cement and aggregates were premixed for 30 seconds in a 50 litre forced circulation mixer for concrete. The mixing water including the admixture was added under stirring within 20 seconds and the concrete mixed for additional 40 seconds. A part of the fresh concrete was immediately used for measuring the flow table spread according DIN 1048 part 1. The remaining concrete was left in the mixer and the flow table spread again measured after 30 and 60 minutes where the concrete was remixed for 10 seconds.

The results of the tests are summarised in table 5.

#### Polymers A in table 5:

Polymers A1 and A5 are modified maleamide-vinyl-copolymers.

Polymers A3 and A4 are copolymers of methacrylic acid with methacrylic ester of methylpolyethyleneglycol.

The W/C ratio is the weight of the cement divided by the weight of the water.

The dosage of the admixtures is in weight % of 40% solutions on cement.

If necessary, the admixtures were defoamed with 0.2% triisobutyl phosphate.

The effect of the inventive admixture comprising polymer A and the polymer of the present invention on the slump life without drastically reduction of the early strength of the concrete is clearly shown in table 5.

Table 5

Polymer A	Polymer of the present invention	Dosage % on cement	W/C	Flow Table Spread (cm)				Compressive strength after 24 hours (N/mm <sup>2</sup> )
				0 min	after 30 min	after 60 min		
Polymer A1	-	0.6	0.47	58	42	39		20.8
Polymer A1	Polymer E14	0.3/0.4	0.47	47	51	51		18.1
Polymer A3*	-	0.8	0.45	56	49	47		25.6
Polymer A3*	Polymer E14	0.64/0.16	0.45	55	52	49		22.3
Polymer A3	Polymer E14	0.48/0.32	0.45	53	53	53		22.2
Polymer A4	-	0.70	0.41	51	47	42		30.3
Polymer A4	Polymer E14	0.56/0.16	0.41	51	48	46		30.2
Polymer A4	Polymer E14	0.35/0.40	0.41	49	49	48		28.9
Polymer A5	-	0.6	0.45	44	36	33		23.1
Polymer A5	Polymer E14	0.30/0.40	0.45	42	42	40		23.6

While there are shown and described presently preferred embodiments of the invention, it is to be distinctly understood that the invention is not limited thereto but may be otherwise variously embodied and practised within the scope of the following claims.